

STUDY ON DEVELOPMENT OF HIGH Mn AUSTENITIC HEAT RESISTING
STEEL -- CHOICE OF BASE COMPOSITION AND THE EFFECT OF
SMALL ADDITIONS OF Ti AND Nb

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T. Shinoda

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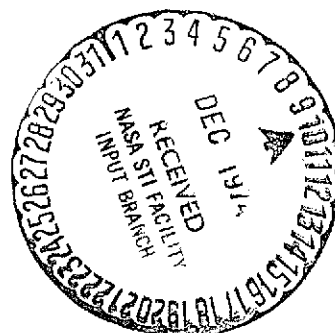
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16. Abstract The most suitable chemical composition of high Mn austenitic stainless steel, developed for high-temperature applications, especially for boiler tubes, has been found to be 18% Cr-6% Ni-8% Mn. This steel's structure is almost wholly austenitic and its creep-rupture strength, oxidation resistance at high temperatures, and hot workability are com- parable to type 304 steel. Small amounts of Ti and Nb, with an optimal (Ti + Nb)/C atomic ratio of 0.1 to 0.5 with 0.2% C, have been simultaneously added to this type of steel to improve the high-temperature strength. The resulting steel has considerably high creep-rupture strength at 600-700°C and is believed to be very economical in high-temperature appli- cations. Depression of coalescence of M ₂₃ C ₆ carbides in grains and on grain boundaries and fine dispersion of carbides within grain boundaries during use at high temperatures con- stitute the mechanism of raising creep-rupture strength due to additions of Ti and Nb.			
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1.11 Introduction

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Large quantities of austenitic stainless steel are used in large-scale boilers for thermal power generating plants and in other fields requiring high strengths at high temperatures. Among them, 18-8 stainless steels occupy a large percentage. These 18-8 type stainless steels ordinarily contain about 10% Ni, and the AISI 316 type steels ordinarily contain 12-13%. For this reason, the manufacturing costs are extremely expensive, and it is believed that there would be a great economic effect if it were possible to replace it with an inexpensive alloy element and to obtain the required high-temperature characteristics.

Among the possible series using no Ni at all would be the Cr-Mn and Cr-Mn-N series. In cases where Ni is used, the Cr-Ni-Mn and Cr-Ni-Mn-N series, in which Mn is used as a partial replacement, are conceivable. However, in cases when the steels are used as heat resisting steels, it is necessary for the austenite phase to remain stable even when heated for prolonged periods at high temperatures. The strength must not decline at high temperatures, and there must be superior oxidation resistance properties. It is believed that the Cr-Ni-Mn series would be suitable as a system satisfying these requirements.

Considerable research has been done in the past concerning Cr-Ni-Mn series austenitic steel [1-14], but in most cases the

* Numbers in the margin indicate pagination in the foreign text.

purposes have been for use as corrosion-resistant steels [7-10] or acid-resistant steels [11-14] rather than as high-temperature materials. These studies were especially active in Europe. At the present time, research is being performed in America, India, China, as well as in Japan [1-6]. However, this research pertains to the Cr-Ni-Mn-N series. In the United States, such steels have even been incorporated in the AISI standards, but the amounts of them in use do not appear to be very great. Thus, most of the countries which are studying the Cr-Ni-Mn series are countries poor in Ni resources, and this is believed to be a problem which will have to be grappled with seriously in our country as well.

2. Base Composition of Cr-Ni-Mn Series Austenitic Steel

2.1. Purposes

As was mentioned in the Introduction, the Cr-Ni-Mn series is believed to be outstanding as heat resisting steel, in particular as steel for boilers. However, for the purpose of improving 18-8 series austenitic steel, it will be necessary to determine an alloy series having a stable austenite phase and superior mechanical properties.

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First of all, since it has been known in the past that the oxidation resistance properties deteriorate in high Mn steels, the Cr content has been made approximately 18% in order to avoid deterioration of the oxidation resistance properties as far as possible. For this reason, we carried out experiments for the purpose of determining the Mn quantity giving a stable austenitic phase while minimizing the Ni as far as possible.

C and N are austenite-forming elements. When they are added to a Cr-Ni-Mn series, they function to stabilize the austenite. However, in these experiments we limited them to the amounts mixed in as impurities and did not specially add any C or N. This was

because we were considering steels for practical purposes which ordinarily have a high C level, and it was also conceivable that N might be added. On the other hand, it was also thought necessary to add ferrite-forming elements to a certain degree, and it was therefore decided that it would be more appropriate to use a series with no additions of C and N as the base composition.

2.2. Steels Tested and Experimental Models

The steels tested were melted in a 50-kg high frequency furnace and were poured into 10-kg steel ingots. The chemical compositions of the melted steels are shown in Table 1. They were divided into 2% Ni, 4% Ni, and 6% Ni series, and Mn was added to a maximum of 22%.

TABLE 1. CHEMICAL COMPOSITIONS OF HIGH Mn AUSTENITIC STEELS MELTED FOR THE EXPERIMENT

Series	Steel	C	Si	Mn	Ni	Cr	P	S	N		
									Sol. N	Insol. N	Total N
A	S 1	0.04	0.48	5.56	2.11	17.91	0.014	0.014	0.0471	0.0001	0.0471
	S 2	0.06	0.44	7.29	1.60	17.64	0.014	0.013	0.0476	0.0001	0.0477
	S 3	0.07	0.40	8.72	2.08	17.29	0.014	0.013	0.0468	tr	0.0468
	S 4	0.07	0.38	10.14	2.00	17.02	0.014	0.012	0.0460	0.0001	0.0461
B	S 5	0.06	0.43	5.72	4.18	18.17	0.012	0.011	0.0341	0.0001	0.0342
	S 6	0.07	0.37	7.78	4.69	17.73	0.013	0.010	0.0351	0.0001	0.0352
	S 7	0.08	0.33	9.30	4.04	17.29	0.012	0.008	0.0375	tr	0.0375
	S 8	0.05	0.55	10.30	3.89	17.30	0.008	0.008	0.0442	tr	0.0444
	S 9	0.04	0.53	14.27	4.11	18.27	0.014	0.011	0.0484	0.0004	0.0488
	S 10	0.04	0.50	16.46	3.93	18.01	0.014	0.010	0.0470	tr	0.0470
	S 11	0.04	0.47	19.10	3.82	17.30	0.014	0.007	0.0410	0.0002	0.0412
	S 12	0.03	0.43	22.00	3.70	16.94	0.014	0.008	0.0432	0.0003	0.0435
C	S 13	0.07	0.43	4.23	6.08	18.08	0.014	0.012	0.0390	0.0001	0.0391
	S 14	0.07	0.38	6.20	5.92	17.82	0.012	0.013	0.0382	tr	0.0382
	S 15	0.08	0.37	7.48	5.87	17.56	0.010	0.011	0.0385	0.0002	0.0387
	S 16	0.08	0.33	8.35	5.71	17.29	0.011	0.011	0.0374	tr	0.0374
	S 17	0.04	0.49	11.75	6.10	18.62	0.017	0.011	0.0416	0.0001	0.0417
	S 18	0.04	0.50	14.18	5.85	18.01	0.016	0.012	0.0418	0.0003	0.0421
	S 19	0.04	0.46	17.26	5.75	17.38	0.016	0.011	0.0418	0.0002	0.0420
	S 20	0.04	0.45	20.20	5.69	17.03	0.014	0.011	0.0382	0.0003	0.0385

Electrolytic iron, electrolytic nickel, and electrolytic manganese were used as the raw materials for melting, but medium carbon ferrochrome was used as the Cr source. The melted steel

ingots were forge-drawn at 1150-1175°C and were used in the experiments described below as 20 mm \varnothing raw materials.

The tests included measurements of the δ -ferrite, structural observations, creep rupture tests, high-temperature twisting tests, hardness measurements, and oxidation resistance tests. The solution heat treatments were performed at 50°C intervals up to 1000-1200°C, and the specimens were water-cooled after being kept at each temperature for 1 hour.

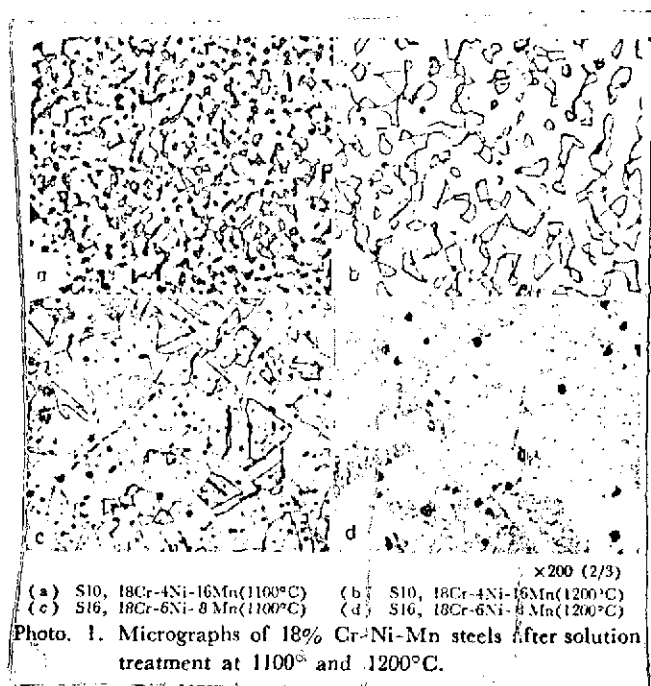
2.3. Experimental Results and Discussion

2.3.1. Structure and Hardness after Solution Heat Treatments

It has been reported that when the Ni quantity is small in Cr-Ni-Mn series, δ -ferrite will appear even when the solution heat temperature is relatively low [6]. Like Ni and Cu, Mn is also an austenite-forming element, but it is far less effective than Ni in stabilizing the austenite. Consequently, since it is anticipated that the austenite stability will decline in alloys with little Ni and a high Mn, we varied the solution heat temperature within the range of 1000-1200°C in order to study the effects of the solution heat temperature on the δ -ferrite quantity. The optical microscopic structures of representative specimens given solution treatment at 1100°C and 1200°C are shown in Photo 1.

The amounts of δ -ferrite in these specimens were measured by the line analysis method. The results are shown in Fig. 1 for those given solution treatment at 1100°C and in Fig. 2 for those treated at 1200°C.

In the A series containing 2% Ni, considerable quantities of δ -ferrite are still observed even when S2 steel with 7% Mn is given solution treatment at 1000°C. The amount increases further



at 1100°C to 36.8% and at 1200°C to 41.9%. In this series, even if about 10% Mn is added, there is a δ -ferrite content of 21.7% even in specimens given solution treatment at 1100°C.

In the B series containing 4% Ni, there is the smallest amount of δ -ferrite when the Mn content is around 10%. However, in specimens given solution

treatment at 1100°C, this will be only 7.8%, and it will be only about 10% in those given solution treatment at 1200°C. If the Mn is further increased, there is a considerable increase of the δ -ferrite, as is shown in Photo 1 (a) and (b).

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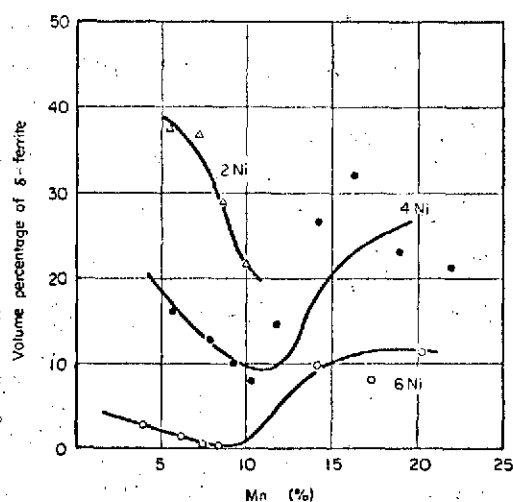


Fig. 1. Change of volume percentage of δ -ferrite vs. Mn content of the steels solution treated at 1100°C.

temperature is increased to 1200°C. However, there will be more δ -ferrite when the Mn is increased. On the basis of these facts it is believed that in the Cr-Ni-Mn series with 18% Cr, the most suitable conditions would be to add 8-10% Mn to 6% Ni.

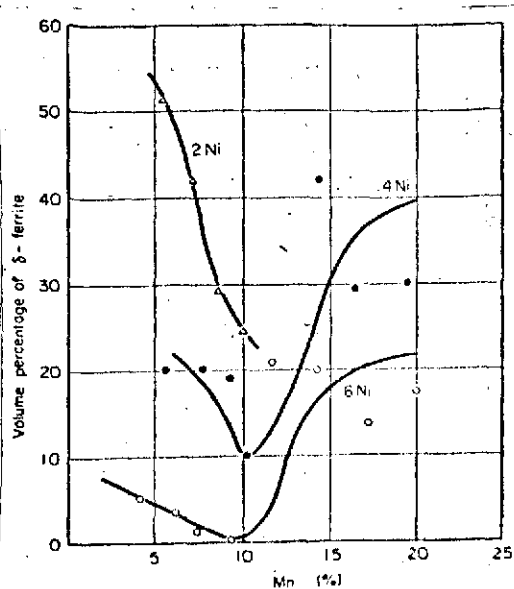


Fig. 2. Change of volume percentage of δ -ferrite vs. Mn content of the steels solution treated at 1200°C.

In Fig. 3 is shown the relationship between the hardness after solution treatment and the Mn content. In all systems, there is a slight decrease in the hardness as the Mn content increases. The hardness also tends to decline generally as the Ni content increases. However AISI 304 steel (hereinafter called "18-8 steel") has a hardness of Hv 140-160 after solution treatment at 1100°C. On an average, the values are higher when compared with this value.

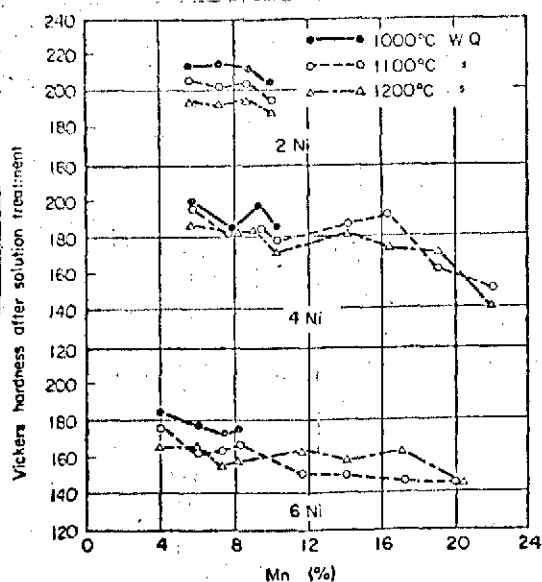
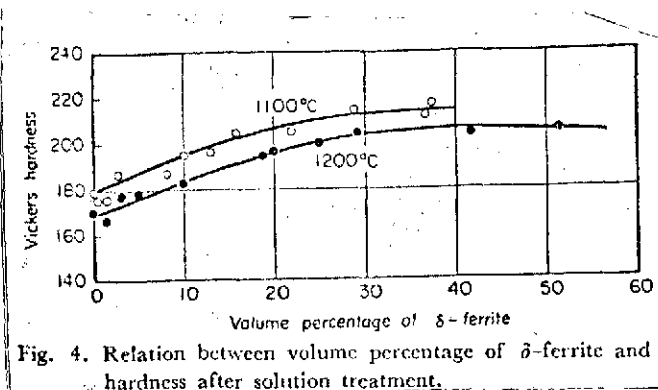


Fig. 3. Change of hardness after solution treatment vs. Mn content.

In Fig. 4 is shown the relationship between the amount of δ -ferrite and the hardness after solution treatment. One can see a tendency for the hardness to increase as the amount of δ -ferrite increases.

As is shown in the preceding, in 6% Ni steels containing 8-10% Mn, the hardness after solution treatment will be less than Hv 180. Such steels are somewhat harder than 18-8 steel, but the difference is only slight.



2.3.2. Hot Twisting Characteristics

It has been reported that the hot workability can be improved by means of Mn [1], and it is also true that much importance is attached to the hot workability of this steel in actual practice.

Therefore, we carried out hot twisting tests to study the hot workability. It is not necessarily appropriate to discuss the hot workability solely on the basis of the results of hot twisting tests. However, since it was thought that they would serve as a sort of yardstick, we compared them with the results for 18-8 steel.

In Fig. 5 is shown the relationship between the twist number to rupture and the testing temperature. In the 2% Ni series, the twist number to rupture increases as the testing temperature rises. /904

In the 4% Ni series, the twist number to rupture remains almost unchanged regardless of the testing temperature; the average number is 5 times; and this value is an extremely low one in comparison with that of 18-8 steel. In the 6% Ni series, just as in the 4% Ni series, there are almost no changes depending on the testing temperature, although generally speaking the twist number to rupture is somewhat higher. The highest value is displayed by 8% Mn steel at 1200°C, and 14% Mn steel generally displays a low twist number to rupture.

In Fig. 6, the twist numbers to rupture of 4% and 6% Ni series are organized in relation to the Mn content. The 6% Ni series displays a higher twist number to rupture on the low-Mn side than the 4% Ni series, and in the 4% Ni series there are almost no changes in the twist number to rupture depending on the Mn content.

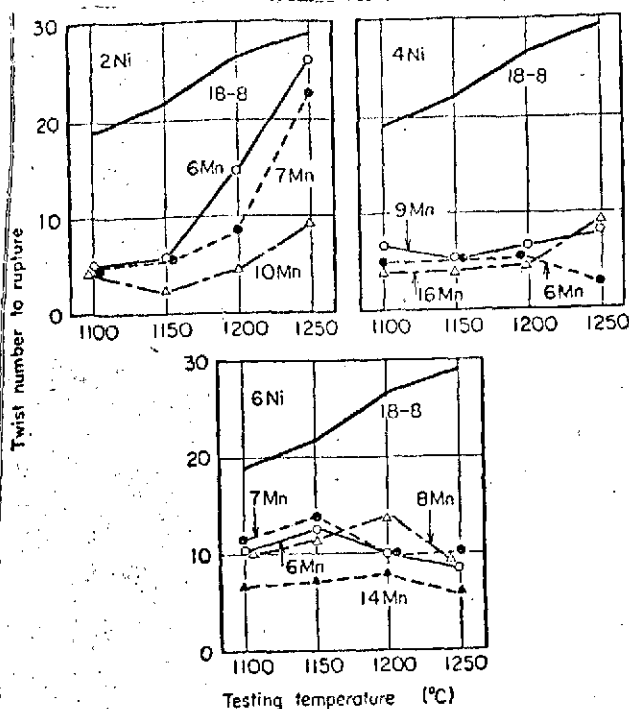


Fig. 5. Change of twist number to rupture vs. testing temperature.

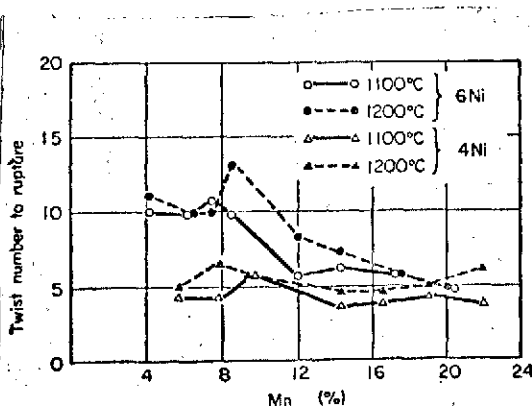


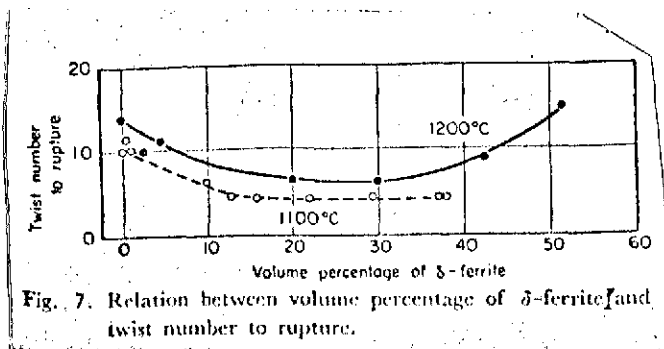
Fig. 6. Relation between Mn content and twist number to rupture.

Fig. 7 in order to study the relationship between the hot workability and the δ -ferrite content. According to the figure, a very small amount of δ -ferrite does not harm the hot workability very severely, but if δ -ferrite of 10-40% is present, the twist number to rupture will decline remarkably. That is, materials containing no δ -ferrite value have a value of 10 twists at 1100°C or 13 twists at 1200°C, but this decreases to about 5 twists when the δ -ferrite content is 25%. However, at 1200°C the twist number to rupture

Furthermore, in the 6% Ni series, there are high values when the Mn content is about 8%. In 6% Ni, it is thought that there is only the austenite phase in the 8-10% Mn region. However, the high Mn steels are quite inferior when compared with 18-8 steel, which has the same austenite phase. Nevertheless, there are no particular difficulties when steel ingots (10 kg) are forged at 1150-1175°C, cracking does

not occur even during rolling, and the deformation resistance also appears to be less than that in 18-8 steel. Thus, one may assume that they have a hot workability which is permissible in actual practice.

The relationship between the twist number to rupture and the δ -ferrite content is plotted in



increases when δ -ferrite of more than 50% is present. In 13% Cr steel [15, 16], at 1200°C the twist number to rupture rises abruptly when there is a δ -ferrite content of 20% or more, but in this steel there is

still no rise at 1100°C even with a content of 40%. Thus, there is a similarity between both steels in the phenomenon in which the twist number to rupture increases when the δ -ferrite content increases above a certain quantity. The δ -ferrite content at which there is a buildup of the twist number to rupture in high Mn steel is a higher value than that in the case of 13% Cr steel, and the buildup also proceeds more leisurely. These differences are no doubt because of differences in the deformability because the amounts of the alloy elements are different in the austenite phase and the ferrite phase between both of the steels.

However, it would be unsuitable for Cr-Ni-Mn steel being treated here to contain large amounts of δ -ferrite on account of the uses for which it is intended. Therefore, it is necessary to select a composition range and temperature at which δ -ferrite will not be produced as far as possible at the hot working temperature. It has also been ascertained empirically that, if there is almost no δ -ferrite, even steel with a twist number to rupture of this degree may be given ordinary hot working.

2.3.3. Oxidation Resistance Characteristics

Since it is said that Mn lowers the oxidation resistance properties, we performed oxidation resistance tests. The tests involved heating for 250 hours at 900°C and then measuring the weight increases. The results are shown in Fig. 8.

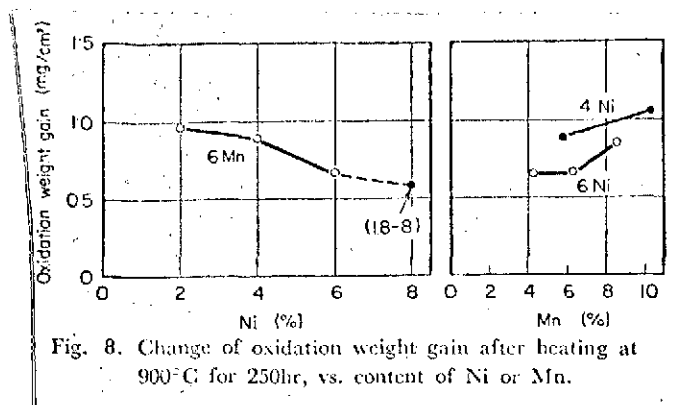


Fig. 8. Change of oxidation weight gain after heating at 900°C for 250hr, vs. content of Ni or Mn.

In cases when the Mn content was kept at 6% while the Ni content was varied, it was found that the 2% and 4% Ni series had oxidation resistance properties which were considerably inferior to those of 18-8 steel, but that

the 6% Ni steel had good values which were little different. On the other hand, when the Ni content was kept constant while the Mn content was varied, it was found that in both the 4% and 6% Ni series, the oxidation weight gain would increase as the Mn content was increased, although the 6% Ni series generally had a smaller oxidation weight gain, and at 4-6% Mn, the values differed very little from those of 18-8 steel. Consequently, it is believed that a Ni content of 6% is necessary also from the viewpoint of the oxidation resistance properties. /905

2.3.4. Creep Rupture Strength

Since the creep rupture strength is especially important among the high-temperature strengths, we performed creep rupture tests for the 4% and 6% Ni series. We used test pieces with parallel parts measuring 6 mm ϕ x 30 mm. Testing was performed using the identical stress at each temperature: 17 kg/mm² at 600°C, 12 kg/mm² at 650°C, 8 kg/mm² at 700°C, and 6 kg/mm² at 750°C, and comparisons were made of the rupture times. The test results at 650°C and 700°C are shown in Fig. 9.

In all the series with constant Ni contents, the creep rupture strengths differed in accordance with the Mn content. In the 4% Ni series, both those undergoing solution treatment at 1100°C and those undergoing solution treatment at 1200°C displayed

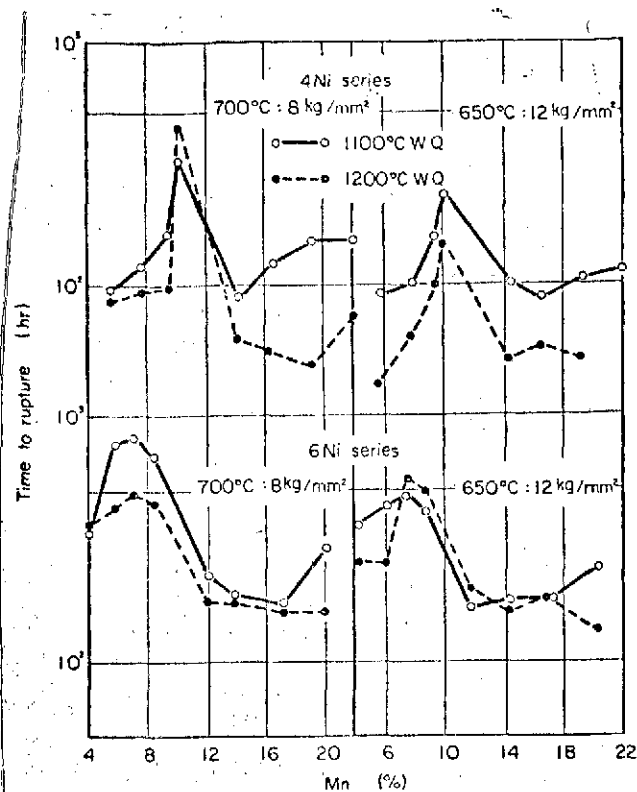


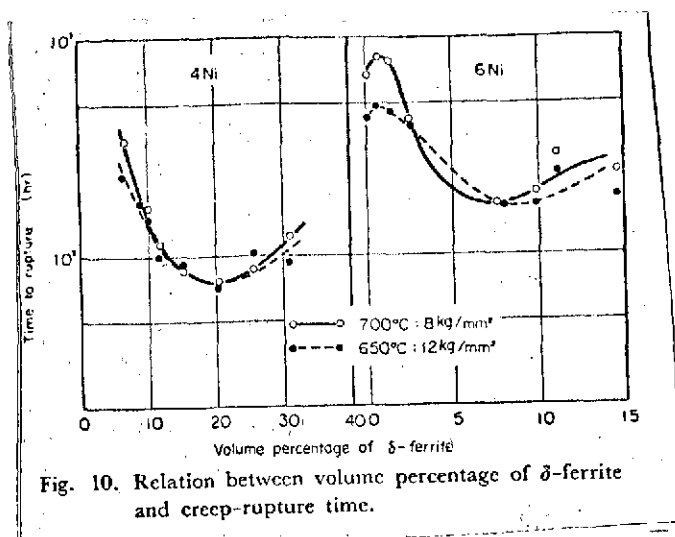
Fig. 9. Change of creep-rupture time vs. Mn content.

their highest strength at an Mn content of about 10% at temperatures of both 650°C and 700°C. When the Mn content was increased beyond this, the strength would decline, and the Mn content giving the maximum strength corresponded to the minimum value of the δ -ferrite content mentioned above. In the 6% Ni series as well, the maximum strength value similarly appeared at a definite Mn content, but, unlike the 4% Ni series, this value was in the vicinity of 6-8% Mn. However, the strength in general was higher in the

6% Ni series than in the 4% Ni series. When we compare the differences depending upon the solution treatment temperatures, the results are better for a temperature of 1100°C.

Since it seems probable that these changes in the creep rupture strength are connected with the δ -ferrite content, in Fig. 10 the creep rupture strength was plotted against the δ -ferrite content on the abscissa.

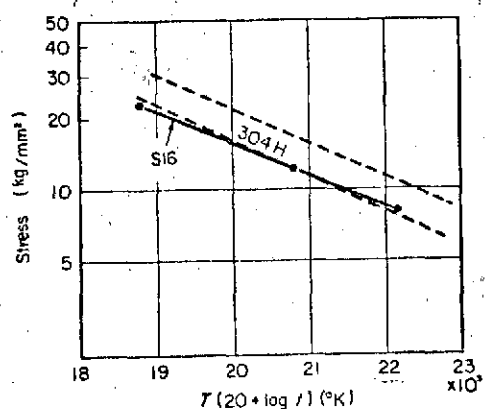
In the 4% Ni series, the minimum value was displayed with a δ -ferrite content of 20%, and the strength was higher the lower was the δ -ferrite content. In the 6% Ni series also, there was a similar minimum strength value, but in this case it was in the vicinity of a δ -ferrite content of 7-8%. There was little increase in the strength even when the content was increased up to the vicinity of 15%. Within the range of a small δ -ferrite content, there is the greatest strength at a content of about



1-2%. In other words, a small amount of δ -ferrite of about 3% or less does not lower the strength, but when the content becomes rather large, there is a sudden drop in the strength.

As has been mentioned above, 6% Ni-8% Mn (S16) steel has the highest creep rupture strength of all the

high Mn steels. Therefore, in order to compare it with 18-8 steel [17], the data were organized according to the Larson-Miller method and plotted in Fig. 11.



Although this S16 steel is believed to be one layer of austenite, its strength almost coincides with the lower limit of the band of 304H steel. As was described in another report [18], there are great fluctuations in the

creep rupture strength of this 304H steel depending upon the charge; charges melted with raw materials having a high virginity and few impurities have a low strength. Since these groups are concentrated in the vicinity of the lower limit of the strength band, it is thought that the lower limit line of the band may justifiably be regarded in itself as the standard strength of 18-8 steel with few impurities. Viewed in this manner, the creep rupture strength of this 18% Cr-6% Ni-8% Mn steel is believed to be equal to that of 18-8 steel. If the Mn content in this series is increased to 14%, the strength will decline somewhat.

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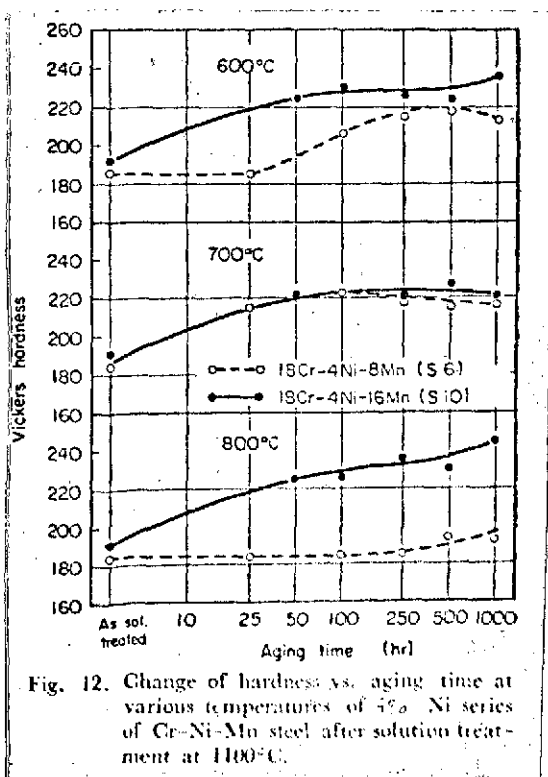
To sum up the preceding, if high Mn austenitic steel consists of one austenite phase, one may conclude that its creep rupture strength is almost the same as that of 18-8 steel.

2.3.5. Structural Changes Caused by Aging

Generally speaking, these steels will undergo structural changes when they are given aging treatment at high temperatures. Thus, in order to find out how these changes occur, we performed heating at 600°C, 700°C, and 800°C up to 1000 hours each. The types of steel tested were 8% and 16% Mn steels of the 4% Ni series and 8% Mn and 14% Mn steels of the 6% Ni series.

The changes in hardness after aging treatment are shown in Figs. 12 and 13. In the S6 steel with an 8% Mn contentt in the

4% Ni series (Fig. 12), at 600°C an increase in the hardness begins before 100 hours, and there is the highest hardness after 500 hours. At 700°C, there is a considerable increase in the hardness before 100 hours, and there are almost no changes after that. The hardness is about Hv 220, which is about the same as the maximum hardness at 600°C. At 800°C, the hardness remains the same as that during solution heat treatment, and there are almost no changes. S10 steel with a 16% Mn content has approximately the same tendency at all temperatures. The hardness rises until about 50 hours, after which it either becomes more or less constant or increases somewhat at



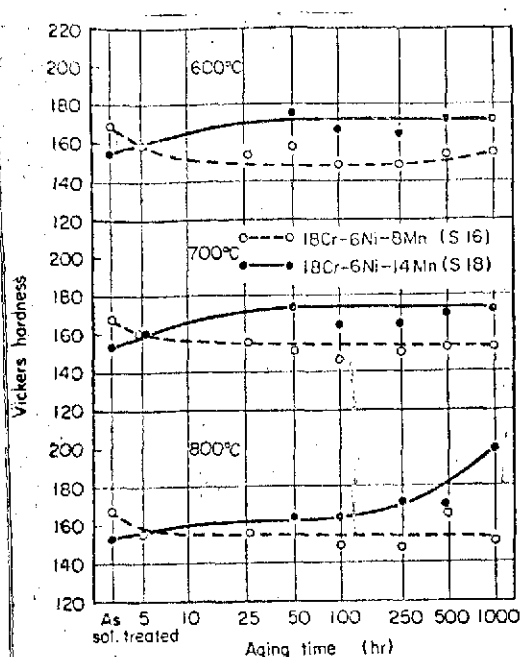
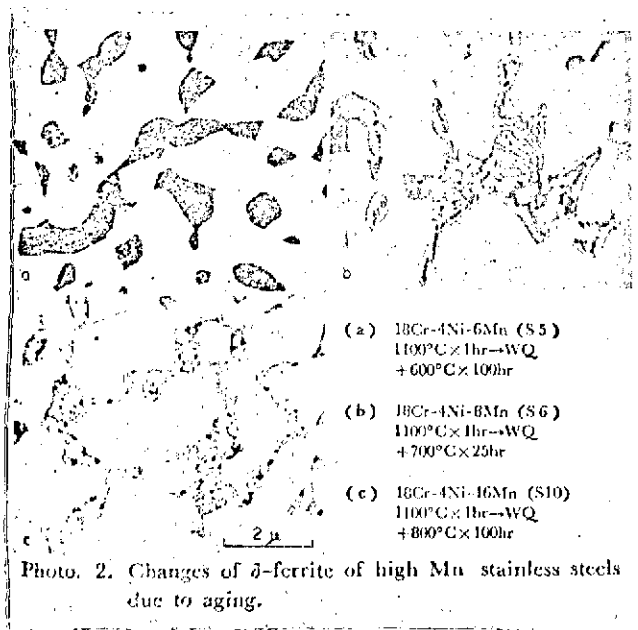


Fig. 13. Change of hardness vs. aging time at various temperatures of 6%Ni series of Cr-Ni-Mn steel after solution treatment at 1100°C.

nearly 1000 hours. The greatest hardness in this case is after 1000 hours at 800°C; the Hv value is about 250.

In the 6% Ni series (Fig. 13), since the steel with the 8% Mn content (S16) is one homogeneous austenite phase, there are almost no changes in the hardness on account of aging. On the contrary, there is even a tendency to become somewhat softer than during the solution heat treatment. Even when the Mn content is increased to 14% (S18), unlike the 4% Ni series, there are no very pronounced changes. However, after 1000 hours at 800°C, there is some hardening to a value of about Hv 200. When these steel specimens after aging treatment were observed under the microscope, no changes at all could be observed in the austenite phase, but it was found that the δ -ferrite had changed considerably. That is, carbides were precipitated inside the δ -ferrite, and they underwent changes together with the temperatures rises or the time increases. In order to illustrate the modes of precipitation of carbides in the δ -ferrite, we show in Photo 2 examples of microphotographs enlarged 1000 times.

At relatively low temperatures such as 600°C (Photo 2 (a)), minute carbides are precipitated in the δ -ferrite, and when the temperature is raised further, they aggregate and assume a form like that in (b). When the temperature rises further to 800°C, aggregation proceeds even further, and coarse carbides are formed in the δ -ferrite, while at the same time, it is believed, some of them are transformed into the σ phase. Consequently, it is not



desirable to have a structure with large amounts of δ -ferrite because brittle σ -phase intermetallic compounds will easily be formed. That is, even if they have a sufficiently high-temperature strength, steels containing δ -ferrite are deemed to be unsuitable for applications in which they will be exposed to high temperatures for prolonged periods of time. /907

2.4. Conclusion

On the basis of various considerations of what has been stated above, in high Mn austenitic steels, if the Ni content is 6% and the Mn content is within the range of 8-10%, it will be possible to obtain an austenite phase containing almost no δ -ferrite even without increasing the C and N particularly. The oxidation resistance properties and creep rupture strength will also be good. Consequently, the most suitable base composition of Cr-Ni-Mn series austenitic steel is 18% Cr-6% Ni-8-10% Mn.

3. Effects of Additions of Minute Quantities of Ti and Nb on the High-Temperatures Strengths of Cr-Ni-Mn Series Austenitic Steels

3.1. Purpose

Since the base composition of the Cr-Ni-Mn series was determined in the previous chapter, we next attempted to improve the high-temperature strength of the alloys of this series. As was previously reported [18], the high-temperature strength of

18-8 stainless steel improves phenomenally when minute quantities of Ti and Nb are added to it. Even though the alloy series may differ, we thought that, on account of their common properties in both being austenitic structures, it might be possible to bring about far-reaching improvements in the high-temperature strength of this alloy series also by adding minute quantities of Ti and Nb. Thus, we performed the following experiments. (In the ensuing sections, 18% Cr-6% Ni-8% Mn steel is called "18-6-8"steel.")

3.2. Steels Tested and Experimental Methods

In these experiments, a rather high C was adopted (the standard value was about 0.2%) in accordance with the same thinking as with 18-8 steel to which minute quantities of Ti and Nb were added (hereinafter called "18-8 TiNb steel"). In order to find out the optimum amounts of Ti and Nb to be added and the effects of their addition, we prepared steel to which no Ti and Nb had been added (M0) as well as four types of steels with various atomic ratios of C/(Ti + Nb) (M1-M4). They were melted with a 50 kg high frequency furnace and made into 50 kg or 10 kg steel ingots. As a result of these investigations, it was discovered that the most suitable value of C/(Ti + Nb) is in the vicinity of 4, ~~just as in 18-8 TiNb steel~~. Next, we established the goal of fixing the value of C/(Ti + Nb) in the vicinity of 4 by the same method, and heated four charges (M5-M8) in which the quantities of Ti and Nb were varied slightly. Furthermore, in order to investigate their characteristics as practical steels, we performed melting by means of a 500 kg [sic] high frequency furnace and manufactured steel tubes by means of a Mannesmann plug mill. This is described in a separate section. The chemical compositions of the experimental steels heated by means of the 50 kg [sic] high frequency furnace are shown in Table 2. /908

The steels for testing either were forge-drawn into 15 mm ϕ round bars at 1150-1230°C or were rolled into 12 mm thick plates

TABLE 2. CHEMICAL COMPOSITIONS OF THE EXPERIMENTAL HEATS (%)

Steel	C	Si	Mn	P	S	Ni	Cr	Ti	Nb	N (sol.)	Ti+Nb* C
M0	0.18	0.57	8.65	0.006	0.010	5.98	17.84	tr	tr	0.0109	0
M1	0.19	0.54	7.84	0.029	0.013	6.02	16.68	0.48	0.63	0.0169	1.11
M2	0.20	0.60	8.10	0.031	0.013	6.08	17.85	0.21	0.21	0.0204	0.50
M3	0.19	0.61	8.10	0.032	0.013	6.16	17.89	0.094	0.11	0.0098	0.19
M4	0.20	0.59	8.10	0.034	0.013	6.13	17.77	0.048	0.055	0.0087	0.065
M5	0.18	0.61	8.12	0.036	0.015	6.34	18.15	0.060	0.11	0.0096	0.16
M6	0.20	0.62	8.10	0.034	0.013	6.34	18.23	0.060	0.20	0.0077	0.20
M7	0.21	0.48	8.62	0.020	0.012	6.28	18.57	0.080	0.11	0.0113	0.16
M8	0.22	0.50	8.38	0.032	0.012	6.22	18.57	0.100	0.20	0.0204	0.23

* Atomic ratio.

with a test rolling mill. After that, they were kept at 1100°C for 1 hour and then given solution heat treatment with water cooling. The M5-M8 specimens after solution treatment were given structural observations and high-temperature tension tests, and all the specimens were given creep rupture tests (600°, 650°, 700°, 750°C). The sizes of the test pieces both for the high-temperature tension tests and the creep rupture tests were 6 mm ϕ x 30 mm in the parallel sections. In the high-temperature tension tests, the tensile velocity was 0.1 mm/min until the proof stress was exceeded; after that, it was 5 mm/min (in both cases the velocities were cross head velocities). (The strain velocities in the parallel sections were about 0.2%/min and 15%/min, respectively.)

Specimens for microscopic examination were cut out of some of the test pieces after creep rupture, and structural observations were performed by the extraction replica method using an electron microscope. In this case, a Virella solution was used for the first-stage corrosion, and a 10% bromine alcohol solution was used for the second-stage corrosion.

3.3. Experimental Results and Discussion

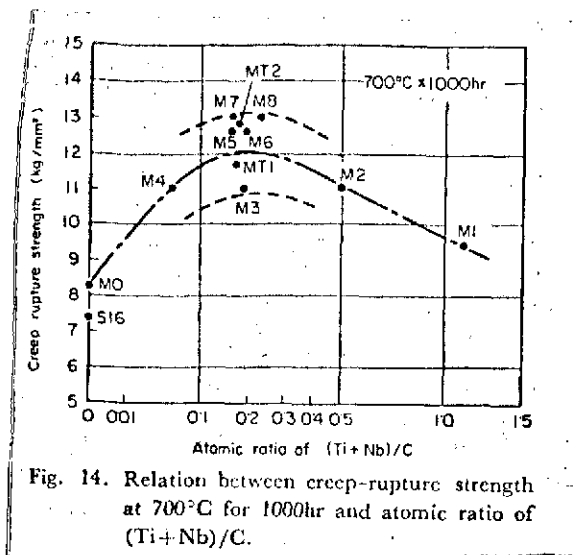
3.3.1. Effects of the Ti and Nb Quantities on the Creep Rupture Strength of 18-6-8 TiNb Steel

As was mentioned in the previous section, we first performed creep rupture tests of the M0-M4 steels in Table 2 in order to find out the suitable amounts of Ti and Nb to use in 18-6-8 steels with Ti and Nb added (hereinafter called "18-6-8 TiNb steel").

The creep rupture tests were carried out at 600-750°C, but the differences in strength were pronounced in the vicinity of 650°C x 1000 hours or 700°C x 1000 hours. At 750°C, the differences were relatively less. Therefore, it was decided to consider the creep rupture strength at 700°C x 1000 hours by organizing the data in terms of the atomic ratio between C and Ti + Nb.

When making comparative studies it was learned that the $C/(Ti + Nb)$ ratio would be infinite when the amounts of Ti and Nb added were zero. This is difficult to express graphically. However, it was found that if the abscissa is calibrated by means of the square root of $(Ti + Nb)/C$, the state of distribution of the strength can be displayed extremely well. Therefore, it was decided to follow this display method in the future.

The relationship between the $(Ti + Nb)/C$ atomic ratio and the creep rupture strength at 700°C x 1000 hours is shown in Fig. 14. Here we also inserted the values of M5-M8, MT1, and MT2, which will be explained below, as well as the values of S16 given in Section 2.3.4 (extrapolated by the Larson-Miller method). It is /909 believed that the difference in strength between S16 and M0 is due to the differences in the C contents. It is clear from this figure that in high Mn austenitic steel, just as in 18-8 steel [18], the maximum value of the creep rupture strength is in the vicinity of a $(Ti + Nb)/C$ atomic ratio of 0.25. However, the



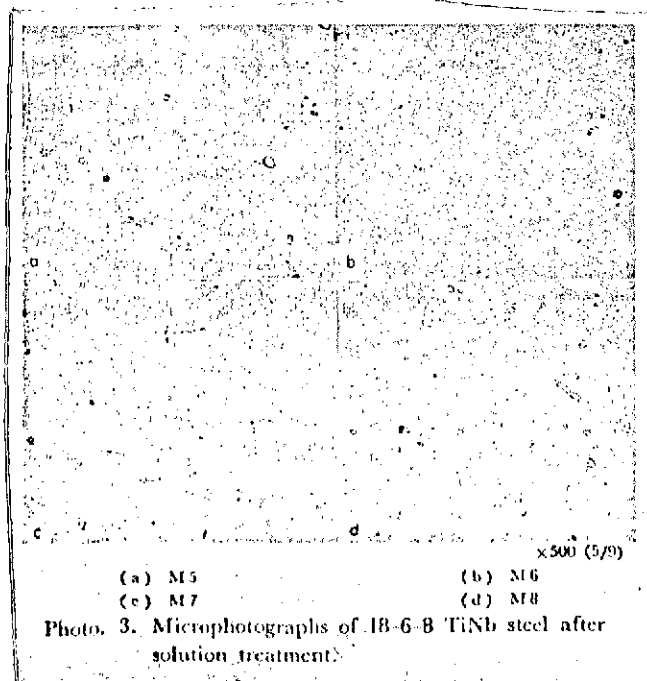
(Ti + Nb)/C ratio displaying this maximum value has a rather broad range of values, and it is thought that values of 0.1-0.5 would be suitable. Consequently, in the subsequent testing, we aimed at a (Ti + Nb)/C atomic ratio in the vicinity of 0.25.

3.3.2. Characteristics of 18-6-8 TiNb Steels

Next, let us describe the characteristics of the standard 18-6-8 TiNb steels (M5-M8) shown in Table 2.

(1) Structure after Solution Treatment

Structures after solution treatment at 1100°C are shown in Photo 3. The photographs show that some δ -ferrite is present in



each type of steel. The particularly large ferrite grains are usually present independently of the recrystallization grain boundary. It is probable that they did not appear during the solution treatment, but rather that they appeared during the forging, since there was a rather high heating temperature at that time.

(2) High-Temperature Tensile Properties

The results of high-temperature tensile testing are shown in Fig. 15. In the figure we also showed, for the sake of comparison, the ranges of variation of the data for AISI 304H and 316H steels given solution treatment at 1100-1150°C. There were almost no differences in the 0.2% proof stress between the charges of these steels, and the values at each temperature up to 750°C were in the vicinity of the upper limit of 316H steel. Although there was a slight decline in 304H and 316H steel at 750°C, there were almost no differences at all in the 18-6-8 TiNb steel within the range of 600-750°C (the values were about 15 kg/mm²).

There were also almost no differences in the tensile strength between the charges, and it is clear that within the range of these experiments, variations in the amounts of Ti and Nb have no effects either on the high-temperature tensile strength or on the proof stress. At normal temperatures, both 304H steel and 316H steel display quite high values of about 73 kg/mm² with respect /910 to 55-62 kg/mm². However, at high temperatures of 600°C or more, their strengths are about the same as that of 316H steel, and there is an improvement of about 50°C, when converted into temperatures, as compared with 304H steel.

As for elongation, there is a margin of variations, but there is no definite tendency between the charges, and as a whole the values are lower than those of 304H and 316H steels. However, even the minimum value is 36%, and it is believed that this is sufficient in actual application.

To sum up the preceding, 18-6-8 TiNb steels have superior high-temperature tensile properties, and the effects of addition of minute quantities of Ti and Nb manifest themselves sufficiently. There are also almost no changes in these strengths when the amounts of Ti and Nb are varied slightly.

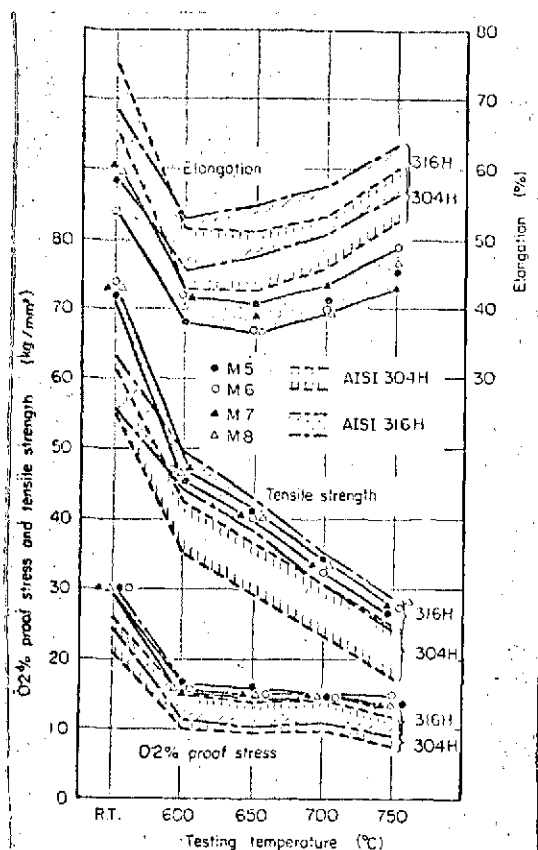


Fig. 15. Tensile properties of 18-6-8 TiNb steel at elevated temperatures.

(3) Creep Rupture Properties

The creep rupture properties of steels M5-M8 are shown in Figs. 16 and 17. The results for the charges (MT1, MT2) in the practical application tests, to be described below, are also shown in these figures.

The creep rupture strengths shown in Fig. 16 at 600-650°C are approximately the same as those of 18-8 TiNb steel [18]. At 700-750°C there is a tendency for them to decline below the strength of the same steel on the long-time side, but on the

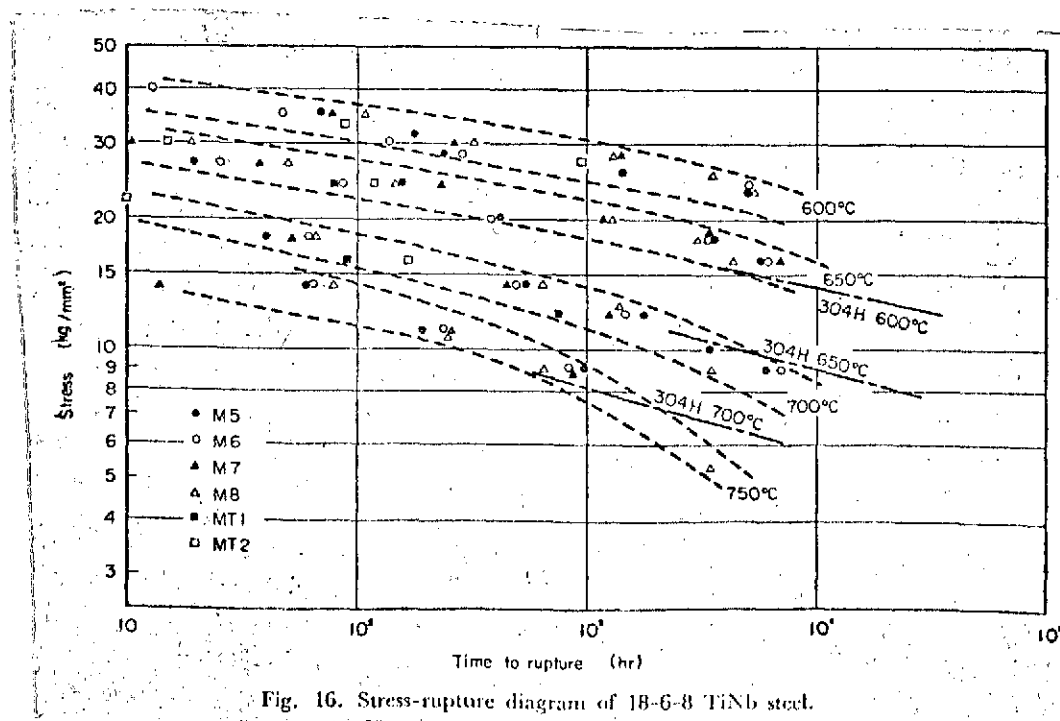


Fig. 16. Stress-rupture diagram of 18-6-8 TiNb steel.

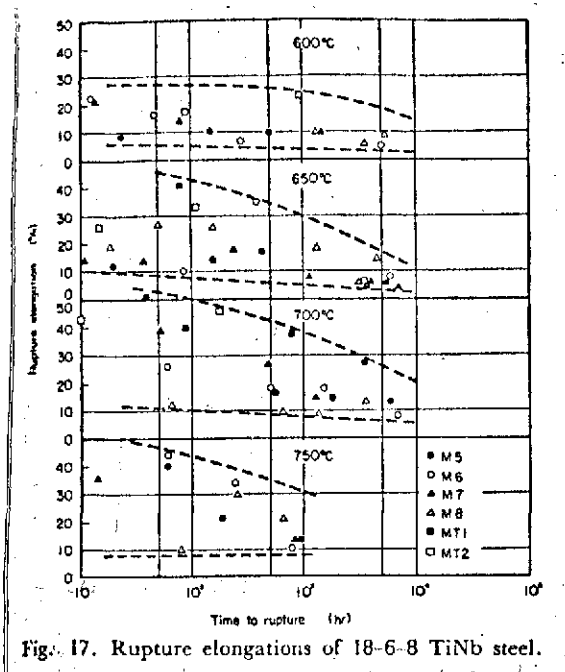


Fig. 17. Rupture elongations of 18-6-8 TiNb steel.

short-time side, they are either about the same or somewhat higher. Consequently, the strength is quite high when compared with 304H steel. For the sake of comparison, the mean values of the creep rupture strengths of 18-8 steel [17] for the long-time side at 600-700°C are shown in the figure, where they are indicated by broken lines with one dot. Within the range of 10,000 hours, the creep rupture strengths of 18-6-8 TiNb steel at 650°C are somewhat higher than the

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strength of 304H steels at 600°C.

The decline in the strength of this steel after prolonged times at 700°C appears to be somewhat pronounced. However, we are currently carrying out testing of this at even longer time periods.

There are some rather high values at the different temperatures on the short-time side in the creep rupture elongations shown in Fig. 17. However, at the longer time in the vicinity of 10,000 hours, all of the values decline considerably, and there is a tendency for almost all of them to be within the range of 5-15%. This is similar to the phenomenon which is generally seen in stainless steels of the 18-8 series [19]. The rupture elongations on the long-time side cannot be estimated by an approach based on the extrapolation method, and the only possible method is to find them by actual long-time testing. At the present stage, the rupture elongations in the vicinity of 10,000 hours

are about 5-15%. These values do not differ very much from those of ordinary 18-8 series stainless steels.

3.3.3. Properties as Practical Steels

In the preceding, we mentioned that 18-6-8 TiNb steels have superior properties as high-temperature steels. However, before putting these steels into actual application, it will be necessary to investigate their workability and other properties necessary for actual uses. For this reason, we heated the steel by means of a 500 kg high frequency furnace. Its chemical composition was as shown in Table 3.

TABLE 3. CHEMICAL COMPOSITION OF 18-6-8 TiNb STEEL USED FOR PRACTICAL EXPERIMENT (%)

Steel	C	Si	Mn	P	S	Ni	Cr	Ti	Nb	N (sol.)	$\frac{Ti+Nb^*}{C}$
MT1	0.17	0.60	7.64	0.030	0.021	5.81	17.56	0.07	0.10	0.0077	0.17

* Atomic ratio

The steel was cast into ingots with a 500 kg mold and was finished by forging into 130 mm ϕ billets. At that time, we collected from the discarded portions samples for testing the hot workability. After peeling of the round billets, steel tubes were manufactured by the Mannesmann plug mill system, and they were finally finished by means of cold drawing into steel tube products with an outer diameter of 50 ϕ 8 mm and a wall thickness of 8.0 mm.

(1) Hot Workability

The hot workability, which is the most important property in practical applications, was assessed by means of hot twist testing and piercing tests [20]. The twist numbers to rupture at 1100-1250°C are shown in Fig. 18. When the results are compared

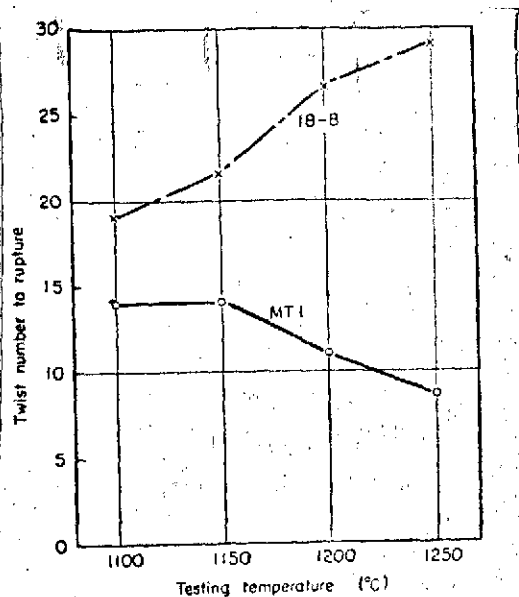


Fig. 18. Results of hot twist test of 18-6-8 TiNb steel (MT1).

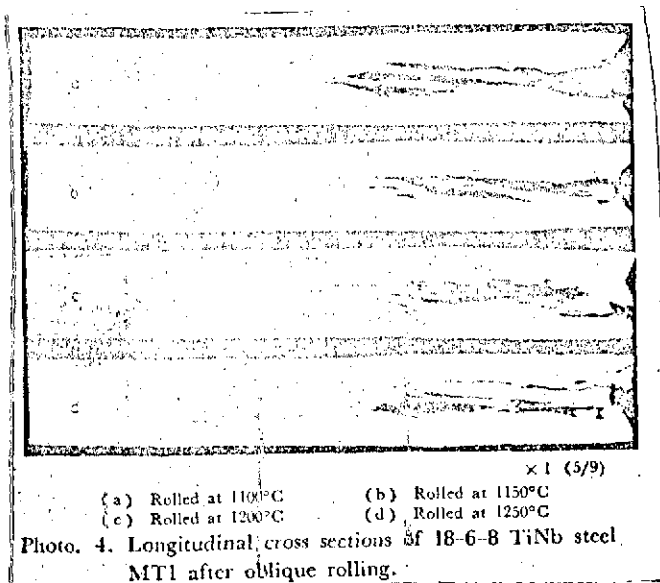
with S16 steel described above (18 Cr-6 Ni-8 Mn, Fig. 5), they are somewhat inferior at 1200°C, but are slightly better at 1100-1150°C. It is clear that there is no decline of the hot workability at 1100-1150°C at least when minute quantities of Ti and Nb are added. It is assumed from these results that a rolling temperature in the vicinity of 1150°C is suitable.

In the piercing tests, tapered billets with a diameter of 25 mm ϕ at one end, a diam-

eter of 30 mm ϕ at the other end, and a length of 150 mm are rolled obliquely on rolls similar to the rolls of a Mannesmann piercing mill. After the test pieces have passed through the rolls, the reduction at one end is 0%. The reduction increases linearly and reaches 20% at the other end. Materials which are unable to withstand working by this rolling will have internal cracking at those parts where the reduction is greater than a definite value. This reduction is called the "critical reduction." In actual pierce rolling, if cracks occur inside the billet because of the draft applied by the rolls before the holes are pierced by the plugs, this will result in internal damages. Consequently, it is desirable for the critical reduction to be as high as possible. It is generally held that it is desirable for it to be at least 5% or more.

Photographs of the longitudinal cross sections of the test pieces are shown in Photo 4. Besides the critical reductions, the shapes of the internal cracks also differ considerably depending upon the materials. It is thought that they also are

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among the factors in determining whether the workability is good or not, but we do not yet have any clear-cut criteria for judging them. The critical reductions at 1100-1250°C measured by these tests are as shown in Table 4. Values of more than 10% are indicated at every temperature. In the steels currently in use, values of 5-6% have been obtained in 304H steels

and of 4-5% in 316H steels, and these steels actually have higher values. The photographs also indicate that there are no particular abnormalities in the shapes of the cracks, and one may judge that the hot workability is good enough. On the basis of these results, it is thought that a working temperature of 1150-1200°C is probably suitable.

On the basis of the test results described above, we performed Mannesmann piercing with a billet heating temperature of 1200°C. The hot-finished steel tubes which had gone through rolling by a plug mill (outer diameter 114 mm, wall thickness 15 mm) had relatively few large damages, but some small damages occurred. Next, they were finished into steel tube products with an outer diameter of 50.8 mm and a wall thickness of 9.0 mm by means of the cold

TABLE 4. CRITICAL REDUCTIONS OF 18-6-8 TiNb STEEL BY OBLIQUE ROLLING TEST

Test temp.	1100°C	1150°C	1200°C	1250°C
Heat No.				
MT1	11.5%	13.3%	13.9%	12.5%

cold Pilger process and cold drawing. The final heat treatment was solution heat treatment of 1140°C x 10 min WQ. The creep rupture test pieces were taken from these products. The creep rupture test results are shown in Fig. 16 above. MT1 was taken from the discarded portions of the forged billets; after forge-drawing, they were given heat treatment of 1100°C x 1 hour WQ. MT2 was taken from the final steel tube products; after cold working, it was given a final heat treatment of 1140°C x 10 min WQ.

(2) Weldability

Concerning the welding of these steels, thought is being given to the development of new welding rods of the double metal system and also to selecting suitable rods from among those available on the market. As a double metal system, we heated steel of the same chemical composition as the base metal in a 50 kg high frequency furnace, made it into wires of 3.2 mm ϕ , and prepared welding test pieces according to the TIG (tungsten inert gas welding) method. As for the products sold on the market, we used rods covered with Iconel 82 and prepared welding test pieces by the arc welding method. Examples of these are given here.

The welding test pieces were plates 12 mm thick. They were each welded according to the methods mentioned above, and creep rupture test pieces were prepared with their welded joints in the center of the parallel part. In each of the welding methods, the welding was performed without preheating, and there were no cracks in the test pieces after welding. Post-heating was not performed, and as-welded pieces were used as the test specimens. The results of the creep rupture tests at 650°C and 700°C are shown in Fig. 19.

Results for test pieces taken from the base metal of the test specimens as well as the strength bands of the 18-6-8 TiNb steel shown in Fig. 16 were also shown in the figure as

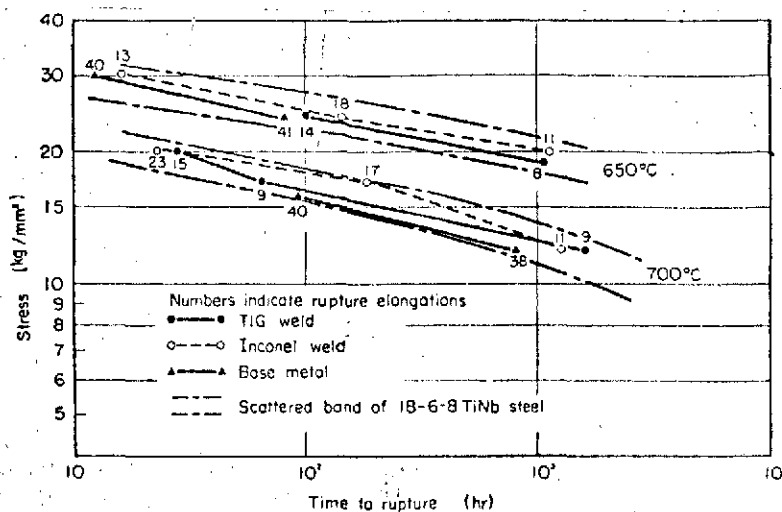


Fig. 19. Stress-rupture diagram of welded specimens of 18-6-8 TiNb steel (NCTI).

comparative data. There were almost no differences in the strength between both welding methods. Although the strength of the welded joints appears to be somewhat higher than that of the base metal, all of these data fit within the strength bands of numerous charges.

The creep rupture elongations are indicated in the figure by numbers. The results indicate that the rupture elongations of the welded joints are considerably lower than those of the base metal. However, as is indicated in Fig. 17, the fluctuations in the rupture elongations under such test conditions are extremely great, and the values of TIG welded joints, which have the lowest of all these values, are the same as about the smallest values of the variations, but no lower. In these cases, the rupture positions may be either the deposited metal, the boundary part, or the base metal, although cases where the ruptures occurred on the deposited metal are somewhat more numerous than the others. When Inconel welding rods are used, the elongations of the deposited metal are extremely great, and there is considerable reduction of the sectional area. However, in the final analysis, in most of the cases the ruptures occurred on the base metal.

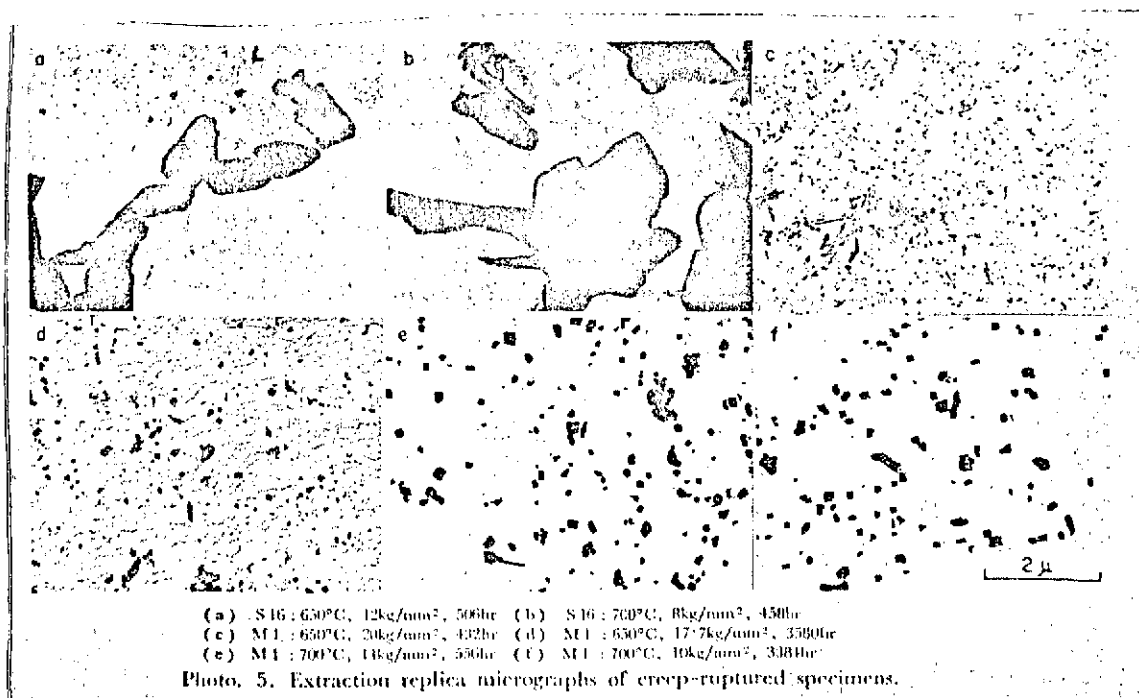
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3.3.4. Microstructure after Creep Rupture

There is a pronounced rise in the creep rupture strength of the steels to which Ti and Nb had been added as compared with high Mn austenitic steels containing no additive elements. In order to find out the mechanism of this strengthening, test pieces after creep rupture were given electron microscopic observations by the extraction replica method.

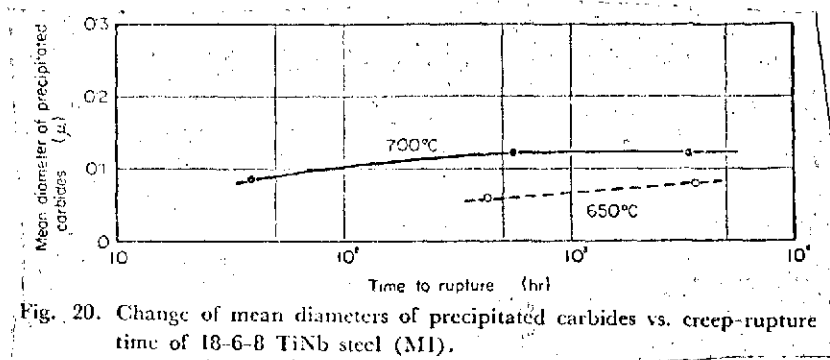
The steels examined were S16 containing no Ti or Nb and M1 containing suitable quantities of them.

In Photo. 5 are shown typical examples of S16 at 650°C and 12 kg/mm² (rupture time 506 hours) and at 700°C and 8 kg/mm² (458 hours); of M1 at 650°C and 20 kg/mm² (432 hours); of M1 at 650°C and 17.7 kg/mm² (3580 hours); of M1 at 700°C and 14 kg/mm² (556 hours); and of M1 at 700°C and 10 kg/mm² (3384 hours).



Even though the C content in Sl6 is not as high as in M1, /914
quite large carbides are precipitated on the crystal grain boundary. As a result of electron beam analysis, they were identified as being $M_{23}C_6$. Besides them, there were almost no other precipitated substances inside the grains. These carbides on the grain boundary appear to grow more and more the higher is the temperature and the longer is the time. Thus, those obtained at 700°C and 458 hours are much larger than those obtained at 650°C and 506 hours. As compared with 18-8 steel, these steels in general have a much faster speed of growth. The sizes of the individual carbide grains at 650°C and 560 hours are approximately 1 μm , and one side is about twice the size of 18-8 steels with a low creep rupture strength and a rapid growth speed of the carbide grains when the latter are subjected to approximately the same conditions (according to measurements made by the writers). This indicates that, even among different types of austenitic steel, when the Mn content is great, the carbide aggregation speed will be great when they are kept at a high temperature. On the other hand, in M1 steel to which suitable quantities of Ti and Nb have been added, there is almost no precipitation of large carbides on the crystal grain boundaries, and the carbides are dispersed in the grains in the form of numerous extremely fine particles. However, at the identical temperatures, the growth of the particles together with the passage of time is extremely limited, and at a temperature of about 700°C there is relatively little growth as the temperature is raised. The particle diameters were measured and expressed quantitatively in Fig. 20.

When the sizes of these particles are compared with those of 18-8 steel [21] and 18-8 TiNb steel [21], at either 650°C or 700°C, the carbide particles of 18-6-8 TiNb steel are smaller than those of 18-8 TiNb steel. Furthermore, at 700°C, the carbide particles of 18-8 steel grow together with the passage of time, but those of 18-6-8 TiNb steel are only slightly larger than those



of 18-6-8 TiNb steel, and the growth is extremely slow after 1000 hours.

If we study the relationship here between the sizes of the carbide particles and the creep rupture strength, even though the 18-6-8 TiNb steel particles generally are larger than the 18-8 TiNb steel particles, their strengths are almost the same and are much better than the strength of 18-8 steel. One can assume that this is because the 18-6-8 TiNb steels, besides having the strength due to dispersion of $M_{23}C_6$ carbides, are also subjected to a certain degree to the solid solution strengthening effect of Mn, and that as a result of this they have come to have a strength of approximately the same degree as 18-8 TiNb steel.

Since the carbide particles in 18-6-8 TiNb steels tend to have a somewhat faster growth speed than in 18-8 TiNb steels, it is anticipated that the differences in their sizes would also expand at an even longer time. This coincides with the tendency for the creep rupture curve to have a somewhat greater inclination, and it would appear especially that the strength should decline considerably at longer than 10,000 hours at 700°C.

In the discussion above we took up only the sizes of the carbide particles, but we did not deal with the distances between particles. This was so for the following reasons. That is, when

viewed microscopically, the sizes of the particles vary relatively little from place to place, but there are considerable variations in their density, that is, in the distance between particles, and it is difficult to make quantitative measurements of the mean values. Besides, with respect to the carbide particle density on the replica surface when the extraction replica method is used, it is possible that the carbide particles may not have been taken in layers with a constant thickness on account of the degree of the corrosion when the replicas are prepared.

However, when the total amount of the carbides is constant, the numbers will be greater and the mean distance between particles will be smaller the smaller is the particle diameter. Therefore, it would seem possible to explain the above-mentioned differences in strength by replacing them with the mean distance between particles, and one may be justified in assuming that the creep rupture strengths of these steels are determined to an extremely great degree by the state of dispersion of the carbides.

3.4. Conclusion

In high Mn austenitic steels in which a base composition of 18% Cr-6% Ni-8% Mn was adopted, if a high C content is adopted and Ti and Nb are added to them so that the atomic ratio of $(Ti + Nb)/C$ will have a value of 0.1-0.5, the creep rupture strength will be extremely high at 600-700°C. This is the same phenomenon as that which occurs when Ti and Nb are added to 18-8 steels. It indicates that at high temperatures the Ti and Nb accelerate the dispersion of the carbide $M_{23}C_6$ and act to suppress its subsequent aggregation.

The 18-6-8 TiNb steels obtained here have approximately sufficient hot workability for use in practical applications; they can be welded without any problems as long as an appropriate

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welding rod is used; and the strength of the joints is the same as that of the base metal. Consequently, they can be said to be inexpensive, extremely economical steels with superior high-temperature characteristics.

4. Summary

The base composition of the Cr-Ni-Mn series was studied for the purpose of developing economical austenitic steels for high temperatures. The desired steels were obtained by adding minute quantities of Ti and Nb to them. The following is a summary of the conclusions reached at each of the stages.

(1) Since almost no δ -ferrite is contained in the Cr-Ni-Mn series, an Ni content of at least 6% is necessary. The Mn content at this time must be 8-10%.

(2) The oxidation resistance properties at high temperatures vary depending upon the amounts of Ni and Mn even when the Cr content is kept constant. If the Ni content is also kept constant, the oxidation resistance properties will decline as the Mn content increases. However, the oxidation resistance properties of 18 Cr-6 Ni-8 Mn steels differ little in comparison with those of 18 Cr-8 Ni steels.

(3) Large amounts of δ -ferrite lower the creep rupture strength. 18-6-8 steels have the same creep strengths as the 18-8 steel charges with lower strengths.

(4) Minute quantities of Ti and Nb, which have a pronounced effect in improving the creep rupture strength of 18-8 steels, also have the same effect on austenitic steels (18-6-8 steels) containing large quantities of Mn. As for the amounts of Ti and Nb added to maintain the maximum creep rupture strength at 600-700°C, the atomic ratio value of $(Ti + Nb)/C$ is within the range of 0.1-0.5.

(5) 18-6-8 TiNb steels have more or less adequate hot workability for all practical purposes, and they can also be welded without any problem. They are extremely economical steels with superior high-temperature characteristics.

In conclusion, the writers express their profound gratitude to Mr. Renpei Yoda of the National Research Institute for Metals for giving us the benefit of his valuable opinions upon the commencement of this research.

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